Aging Effects of Environmentally-Friendly Cleaners on Adhesive Bond Integrity

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Abstract: Because of the 1990 Clean Air Act Amendment many chlorinated solvents are being phased out of use in manufacturing industries. Replacement of the ODC (ozone-depleting chemicals) with less volatile, non-ozone depleting cleaners has been extensively studied over the past nine years at Thiokol Propulsion, Cordant Technologies.

Many of the non-ODC cleaners contain compounds that can potentially degrade over time under conditions of high temperature, humidity and exposure to light. The chemical composition of environmentally conditioned cleaners and the subsequent effect on aluminum/amine-cured epoxy bond integrity as measured by Tapered Double Cantilever Beam were evaluated.

From this study it is observed that moisture content increases for those cleaners containing polar compounds. Non-volatile residue content increases as stabilizers are depleted and the chemical compound limonene is oxidized. A change in aluminum/ amine-cured epoxy bond fracture toughness is observed as some of these cleaners age with increases in moisture and NVR content.

1 INTRODUCTION

The chemical stability of cleaners in the manufacturing area is an important concern as many cleaners are used over a six-month period after removal from the vendor container and stored in temporary hand-use applicators/bottles. A principal constituent of many of the ODC-free cleaners evaluated in this study is the terpene hydrocarbon, limonene. Analytical testing indicates limonene chemically oxidizes over time with exposure to oxygen. This decomposition is accelerated in the absence of antioxidants and is a concern to the cleaners' shelf life and the effect on bonding.

2 EXPERIMENTAL

2.1 Cleaners

Six cleaners were selected from the candidates that are considered acceptable alternatives to 1,1,1 trichloroethane for hand-wipe cleaning production components. These cleaners are listed in Table 2.1. Many of the cleaners contain limonene as part of their composition. Note the percentage of limonene varies from 100 to 8 percent depending on the cleaner. A few of these cleaners contain the stabilizer BHT (butylated hydroxytoluene) at various levels. Dipropylene glycol methyl ether (DPGME) is also a cleaner component along with 1TB2P (1-t-butoxy-2-propanol) and N-methyl pyrrolidone. Two of the cleaners contain a mixture of more non-polar components, hydrocarbons.

2.2 Storage Environment

Storage conditions were selected to not only represent typical conditions found in the manufacturing areas but also, in the worse case, induce high levels of non-volatile residue (NVR). The mild (typical manufacturing condition) environment was selected as 22°C, less than 10% R.H. and samples stored in the dark. For harsh conditions, the bottles were stored at 40°C, 50 % R.H. and under constant exposure to fluorescent lighting.

2.3 Moisture

Moisture analysis was conducted per the ASTM E203 Standard Test Method for Water Using Karl Fischer Reagent.

2.4 Non-volatile Residue

Cleaner NVR content was measured by evaporation of the volatile fraction in a forced draft oven. The residue is an empirical measurement defined by the evaporation conditions (40°C) and defined as any material that does not evaporate after four hours in a forced draft oven. These residues may be the result of bottle dissolved contaminants/ plasticizers or solvent degradation.

2.5 Bondline Fracture Toughness

The fracture toughness of an aluminum/epoxy bondline cleaned with the selected ODC-free cleaners was measured using aluminum Tapered Double Cantilever Beam (TDCB) test specimens. The TDCB configuration was selected to evaluate the interfacial effect cleaners have on an epoxy aluminum bonded joint. As a baseline surface preparation, the aluminum substrates were degreased with 1,1,1 trichloroethane and grit blasted.

The effect of cleaner residue on bondline fracture toughness was studied along with the ability of the aged cleaner to remove grease. Grease was applied to a selected number of samples, and after 24 hours at 40°C the grease was removed from the aluminum substrates with the appropriate ODC-free cleaner. These samples were compared to those that were not grease contaminated yet were wiped with the selected cleaner.

TIGA 321 (an amine-cured epoxy adhesive) was applied to a 0.050-inch thickness on the aluminum substrate and cured for 48 hours at 40°C. The TDCB specimens were tested at room temperature at 0.005 ipm.

3 RESULTS AND DISCUSSION

Initially the moisture content of BA1, PL4 and BA4 is higher compared to the other cleaners (Figure 3.1). This is most likely due to the hydrophilic nature of the cleaner components. Both BA1 and PL4 contain an alcohol component while BA4 and PL4 contain glycol methyl ether. Over time, under high humidity conditions, these cleaners continue to increase in moisture content and have higher levels than the other cleaners.

Cleaner NVR content also increases during storage under harsh conditions (Figure 3.2). PCG and BA1 both contain the limonene component without a stabilizer and thus at zero time have rather high NVR levels compared to the other cleaners. These cleaners with limonene and no stabilizer immediately begin to form NVR while those cleaners with stabilizer (PRP, PL4, PFD) remain unchanged for several weeks until the stabilizer is depleted. The cleaner with no limonene (BA4) remains consistent with low NVR content.

Bondline fracture toughness changes dramatically over a 13-week period for those cleaners stored under harsh conditions. Initially (Figure 3.3) the bondline fracture toughness is quite low for all samples whether grease-contaminated then cleaned or just cleaned. Most fracture toughness values are below 600 J/m^2.

Only the BA1 and PL4 (to a lesser extent) cleaners show significantly higher values for zero-time samples without grease contamination. Both BA1 and PL4 contain the more polar alcohol component. In any case, the baseline (TCA vapor degrease with grit blast) surface preparation demonstrates a significantly higher bondline fracture toughness compared to the cleaner wiped surfaces. Better bondline fracture toughness can be obtained with a freshly grit blasted surface without cleaner residue.

Failure modes at zero time testing however are significantly. Greased then cleaned samples demonstrate interfacial failure between the adhesive and the aluminum while cleaned samples (no grease) demonstrate thin film cohesive in the adhesive and stress whitening of the adhesive. These failures occurred no matter which cleaner was evaluated.

At three weeks (Figure 3.4), BA1 (and to a lesser extent PL4) continues to demonstrate higher bondline fracture toughness values (without grease contamination). The other cleaners also show an increase in values compared to those observed at zero-time testing. As with the zero-time values, the baseline (no cleaner wiped) surfaces demonstrate significantly higher bondline fracture toughness and there continues to be no significant difference between greased and no greased samples.

After thirteen weeks (Figure 3.5) under harsh conditions, all cleaners demonstrate a significant increase in bondline fracture toughness from zero-time values. Failures occur cohesively in the adhesive with stress whitening of the adhesive prevalent. In many cases, the values are similar to the baseline (no cleaner wiped) surfaces.

4 CONCLUSIONS

Bondline fracture toughness energy values would indicate the cleaners with the more polar component, 1-t-butoxy-2-propanol, demonstrate significantly higher values at zero-time testing. Over time, as the other cleaners also become more polar, they also demonstrate an increase in bondline fracture toughness energy.

The data collected at 13-weeks would indicate that oxidized limonene products have more influence on the bondline fracture toughness energy compared to moisture content. The BA4 cleaner with little NVR content (and yet significant moisture levels) demonstrates lower bondline fracture toughness energy compared to the other cleaners. BA4 does not clean grease off aluminum parts as well as PCG with high levels of NVR content.

Table 2.1 Cleaners and Composition

Cleaners***	Abbreviation	Limonene (%)	BHT (ppm)	DPGME (%)	HC (%)	MP (%)	1TB2P (%)
BIOACT® PCG	PCG	100					
RE-ENTRY® PREPSOLV	PRP	100	278				
RE-ENTRY® PLUS 4 SOLVENT	PL4	75	198	9		5	11
BIOACT® 113	BA1	36					64
PF™ Solvent	PFD	8	17		92*		
BIOACT® 145	BA4			27	73**		

* = C_{10} to C_{14} hydrocarbons
** = Mixed aliphatic hydrocarbons (C_9 to C_{13} branched and cyclic).
*** = all cleaners are manufactured by Petroferm except for "PF" Degreaser that is manufactured by PT Technologies

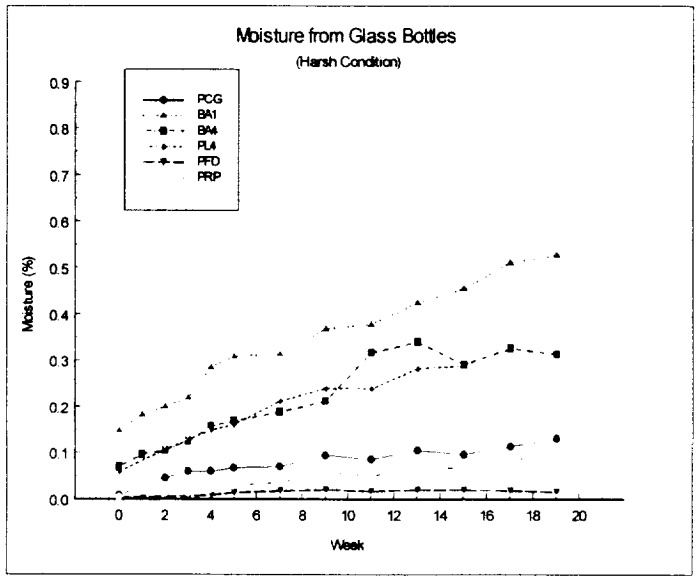

Figure 3.1 Cleaner Moisture Content over Time.

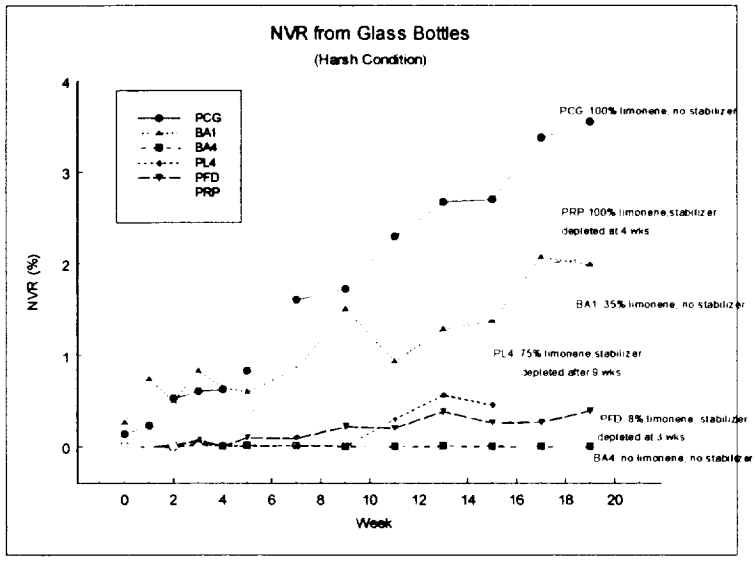

Figure 3.2 Cleaner NVR Content under Harsh Conditions.

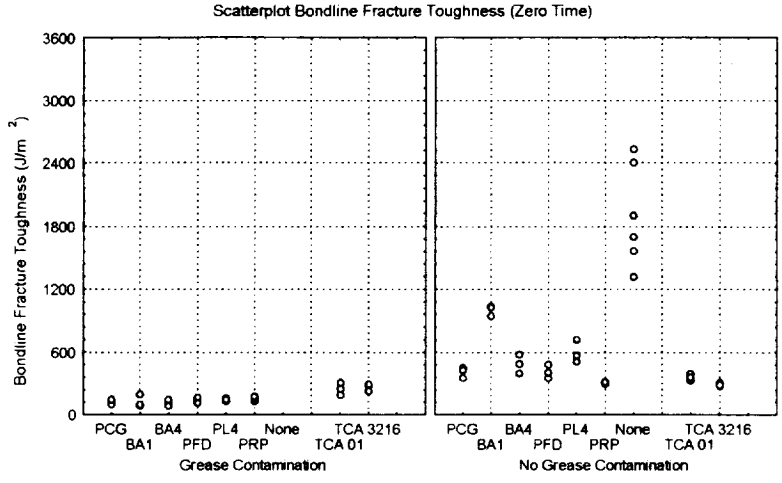

Figure 3.3 Zero-time Bondline Fracture Toughness

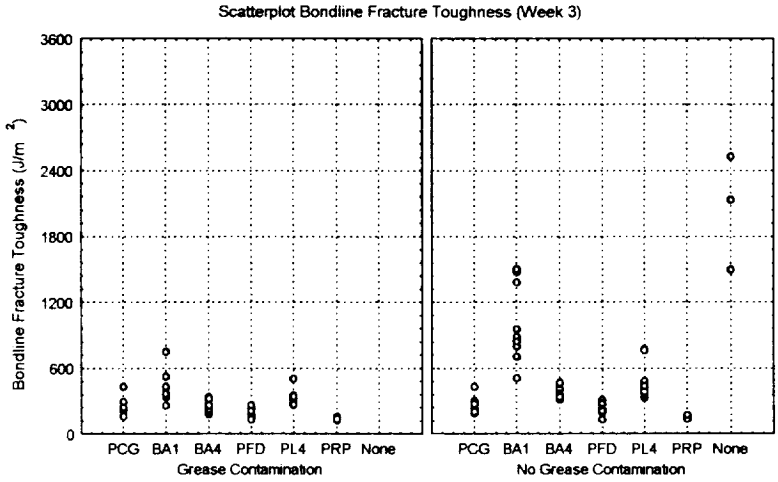

Figure 3.4 3-Week Bondline Fracture Toughness

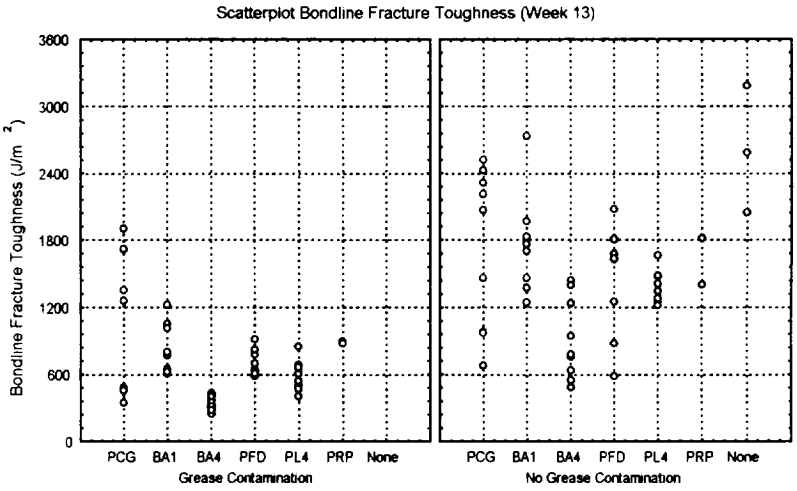

Figure 3.5 13-Week Bondline Fracture Toughness